

The Forced Gas Sweeping Process for Semibatch Melt Polycondensation of Poly(ethylene terephthalate)

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ABSTRACT: The experimental and modeling studies are presented on the melt polycondensation of poly(ethylene terephthalate) by a gas sweeping process. In this process, low molecular weight prepolymer is polymerized to a higher molecular weight polymer in a molten state at ambient pressure as ethylene glycol is removed by nitrogen gas bubbles injected directly to the polymer melt through a metal tube. In the temperature range of 260–280°C, the rate of polymerization by the gas sweeping process is quite comparable to that of conventional high vacuum process. The effects of nitrogen gas flow rate and reaction temperature on polymerization rate and polymer molecular weight were investigated. Polymer molecular weight increases with an increase in gas flow rate up to certain limits. A dynamic mass transfer–reaction model has been developed, and the agreement between experimental data and model simulations was quite satisfactory. The effect of ethylene glycol bubble nucleation on the polymerization has also been investigated. It was observed that the presence of nucleated ethylene glycol bubbles induced by the bulk motion of polymer melt has negligible impact on the polymerization rate and polymer molecular weight. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 81: 1388–1400, 2001

Key words: melt polycondensation; poly(ethylene terephthalate); forced gas sweeping process; polymerization; mass transfer–reaction model; bubble nucleation

INTRODUCTION

Melt polycondensation processes are used industrially to manufacture thermoplastic engineering polymers such as poly(ethylene terephthalate) (PET) and copolymers. With a rapidly growing demand for PET in many new and diversified

applications, PET continues to be one of the world's fastest growing polymers (e.g., 12.9%/year growth through 2002¹). As a result, a quest for more efficient and advanced industrial PET process technology continues.

PET has been manufactured industrially by stagewise high vacuum melt polycondensation processes. Currently, PET is produced starting with either terephthalic acid or dimethyl terephthalate and ethylene glycol. PET in melt processes is formed by the reactions between reactive functional end groups in the presence of soluble metal oxide catalysts such as Sb_2O_3 . In the first stage, monomers are polymerized to low molecular weight oligomers with metal acetate catalyst

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(e.g., zinc acetate) in a series of mechanically stirred tank reactors. The low molecular weight oligomers are polymerized to prepolymers of relatively low molecular weight (number average degree of polymerization $X_n = 15\text{--}30$) and then they are further polymerized in a finishing stage to higher molecular weight polymers. Solid state polymerization may also be employed to increase X_n to above 100. In addition to the main polycondensation reaction, many side reactions are known to occur, resulting in undesired side products such as aldehydes, diethylene glycol, and vinyl end groups.

Since the polymerization reactions are reversible, it is necessary to remove low molecular weight reaction by-products (or condensates) from the reacting melt phase to shift the equilibrium toward the chain growth reaction. In PET manufacturing, ethylene glycol is the major reaction by-product to be removed. It is well known that mass transfer in polymeric solutions or melts by molecular diffusion of a small molecular weight compound such as ethylene glycol is a comparatively slow process. Hence, very large surface areas for interfacial mass transfer are required or pressure is reduced. In conventional melt polycondensation processes, high vacuum (1–3 mm Hg or less) is usually applied to remove volatile reaction by-products and various types of reactor designs are used in industrial processes (e.g., rotating disk reactors, screw reactors, caged reactors, wiped film reactors, etc.). The primary objective in designing such reactors is to create as large a gas–liquid (melt) interfacial area as possible to facilitate the removal of condensation by-products. The application of high vacuum demands high energy cost because low molecular weight condensation by-products must be removed from an increasingly viscous polymer melt as the polymer molecular weight increases. Such processes also require high cost vacuum equipment, multistage steam jets, and mechanical parts to minimize leakage of air into the system. Condensates from the steam jets and organic by-products often end up as a waste water stream requiring costly decontamination.^{2–9}

In a polymer devolatilization process, a stripping agent immiscible with the polymer is often introduced into the polymeric solution. Then, monomer or solvent molecules diffuse to the surface of the gas bubbles composed mainly of the stripping agent. These bubbles will grow and ultimately rupture. This concept can be applied to the melt PET process, i.e., inert gas may be in-

jected to the melt phase to remove condensation by-products. Recently, several patent literature report that the polymer (PET) molecular weight can be increased at ambient pressure by removing ethylene glycol with inert gas such as nitrogen.^{2–9} Although the idea of using inert gas to remove condensation by-products was reported many years ago before these recent patents were disclosed, no commercialization of the PET process using such technique has followed. The publications by Bhatia^{2–9} indicate that this technique is of renewed industrial interest. For industrial applications of the ambient pressure process, there are a few factors to be considered. For example, the quantity of inert gas should not be too large, inert gas velocity may not be too high, and the contact between the inert gas and the polymer melt in the reactor should be adequate and uniform.^{2–9}

Although the finishing stages of low pressure melt PET polycondensation processes have been modeled and analyzed by several workers,^{10–16} little has been reported on the forced gas sweeping process (GSP) except for patent literature. In this paper, we shall present both experimental and theoretical modeling studies on melt polycondensation of PET by the gas sweeping technique.

EXPERIMENTAL

We have carried out a series of experiments to investigate the melt polycondensation of PET by forcing heated inert gas (nitrogen) to flow in a viscous polymer melt to remove condensation by-product. The reactor system consists of a Pyrex glass tube reactor and a glass heating jacket in which high temperature fluid is circulated to keep the reactor temperature at its desired set point. The reactor is charged with a predetermined amount of prepolymer particles of known molecular weight [X_n (degree of polymerization) = 9]. As the reactor tube is placed in the heated glass jacket assembly, the prepolymer particles melt in about 2–3 min. Then, dehumidified and heated nitrogen gas is supplied at constant flow rate to the bottom portion of the reactor through a small diameter (0.318 cm) metal tube inserted in the center of the glass reactor. The entire gas supply line is heated and heavily insulated. The feed gas is preheated to the jacket temperature. Since it was difficult to insert a thermocouple in the reaction tube without interfering the flow of gas bubbles, we controlled the heating jacket tempera-

ture during the polymerization experiments. Table I shows the actual melt temperature in the reaction tube and the corresponding jacket temperature for various gas flow rates. Note that there are small differences in temperatures between the reactor tube and the heating jacket at different nitrogen gas flow rates.

The prepolymer (donated by Allied Signal Company) used in our experiments contains a small amount of catalyst and no additional polymerization catalyst is added. A small amount of polymer sample is taken at every 30 min for analysis. The molecular weight of PET was measured by gel permeation chromatography using a chloroform/hexafluoroisopropanol mixture as a solvent with a single linear column (Phenomenex) and a UV detector.

Mass Transfer–Reaction Model

In the following, we shall present a mass transfer–reaction model for the synthesis of PET by the inert gas sweeping process. Let us consider a semibatch melt polycondensation reactor. The reactor is initially charged with molten prepolymer and noncondensable inert gas is supplied continuously to the reactor. Gas bubbles formed at the tip of a gas injection tube (or nozzle) rise through the polymer melt. Ethylene glycol molecules generated by polycondensation in the melt phase diffuse to these rising bubbles. As ethylene glycol is removed from the melt phase, the forward chain growth reaction is promoted and polymer molecular weight increases. Figure 1 shows a schematic of the reaction and mass transfer processes in the melt polycondensation of PET in presence of inert gas bubbles. In developing the model, we assume that the reactor temperature is constant and that bubbles are spherical and of uniform size. It is also assumed that each bubble has the same residence time in the reactor.

Table I Reaction and Jacket Temperatures at Different Gas Flow Rates

Jacket Temperature (°C)	Reactor Temperature (°C)			
	1.4 mL/s	5.2 mL/s	13.0 mL/s	20.8 mL/s
260	260	258	254	251
280	280	278	276	274

^a Inlet gas temperature = jacket temperature.

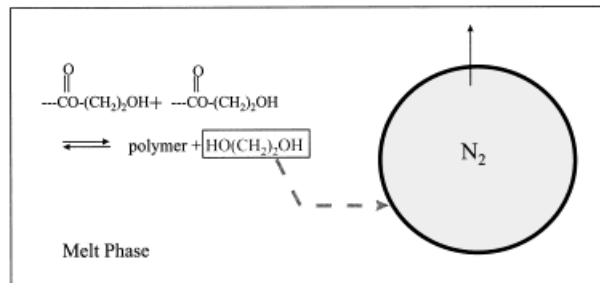


Figure 1 Mass transfer from melt phase to inert gas phase.

The molar mass transfer rate of ethylene glycol (EG) per unit volume of the melt phase is expressed as

$$N_{\text{EG}} = (k_L a)_m ([\text{EG}]_m - [\text{EG}]_m^*) \\ = (k_L a)_g ([\text{EG}]_g^* - [\text{EG}]_g) \quad (1)$$

where $(k_L a)_m$ and $(k_L a)_g$ are the mass transfer parameters for the melt phase and the gas phase, respectively (N_{EG} : molar mass transfer rate of EG in mol/cm³ s; k_L : mass transfer coefficient in cm/s; a : specific mass transfer area in cm²/cm³; subscript m : polymer melt phase; subscript g : gas phase).

The concentrations of ethylene glycol at the gas–liquid interface are related by the following equation:

$$[\text{EG}]_g^* = m[\text{EG}]_m^* \quad (2)$$

where m is the vapor–liquid equilibrium coefficient. Then, from eqs.(1) and (2) we obtain

$$[\text{EG}]_m^* = \frac{(k_L a)_m [\text{EG}]_m + (k_L a)_g [\text{EG}]_g}{(k_L a)_m + m(k_L a)_g} \quad (3)$$

Therefore, the molar transfer rate is expressed as

$$N_{\text{EG}} = (m[\text{EG}]_m - [\text{EG}]_g) \left\{ \frac{1}{(k_L a)_g} + m \frac{1}{(k_L a)_m} \right\}^{-1} \quad (4)$$

If the mass transfer resistance in the gas phase is far smaller than the mass transfer resistance in the melt phase, the above equation is reduced to

$$N_{\text{EG}} = (k_L a)_m \left([\text{EG}]_m - \frac{1}{m} [\text{EG}]_g \right) \quad (5)$$

The mass balance equation for ethylene glycol in the melt phase takes the following form:

$$\frac{d(V_m[\text{EG}]_m)}{dt} = V_m r_{\text{EG}} - V_m (k_L a)_m \times \left([\text{EG}]_m - \frac{1}{m} [\text{EG}]_g \right) \quad (6)$$

V_m is the volume of the melt phase in cm^3 and r_{EG} is the rate of ethylene glycol formation. Note that if the bubbles are of uniform size, the specific interfacial area, a (in cm^2/cm^3 melt), is NS_g^*/V_m , where N is the total number of gas bubbles in the reactor and S_g^* is the surface area of a gas bubble. Both N and bubble size are dependent upon the gas flow rate and melt viscosity that changes during the course of polymerization.

Now let us suppose that inert gas is injected to the reactor at a constant volumetric flow rate of Q_g (in cm^3/s). If the bubble phase volume (or gas holdup) in the reactor is assumed constant and the gas bubbles are well mixed with the melt phase, the mass balance of ethylene glycol in the gas phase is expressed as

$$V_g \frac{d[\text{EG}]_g}{dt} = V_m (k_L a)_m \left([\text{EG}]_m - \frac{1}{m} [\text{EG}]_g \right) - Q_g [\text{EG}]_g \quad (7)$$

where V_g is the total volume of gas bubbles in cm^3 . Since ethylene glycol is continuously removed from the melt phase, there will be a small decrease in the melt phase volume. However, if such a small change in the melt phase volume is ignored, eqs. (6) and (7) are reduced to

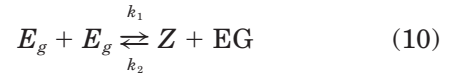
$$\frac{d[\text{EG}]_m}{dt} = r_{\text{EG}} - (k_L a)_m \left([\text{EG}]_m - \frac{1}{m} [\text{EG}]_g \right) \quad (8)$$

$$\frac{d[\text{EG}]_g}{dt} = \frac{V_m}{V_g} (k_L a)_m \left([\text{EG}]_m - \frac{1}{m} [\text{EG}]_g \right) - \frac{Q_g}{V_g} [\text{EG}]_g \quad (9)$$

These equations indicate that the gas holdup, the melt phase volume, and the mass transfer parameter are the major model parameters.

In the polymerization of PET, many side reactions occur. In this work, however, we shall focus on the development of polymer molecular weight

in the gas sweeping process. Thus, we consider the main polycondensation reaction only, which is represented as



where E_g is the hydroxyl end group, Z is the diester group, and k_1 and k_2 are the forward reaction rate constant and reverse reaction rate constant, respectively, both in L/mol min . The rate of reaction in the melt phase is expressed as

$$r = k_1 [E_g]^2 - 4k_2 [Z][\text{EG}]_m \quad (11)$$

Since the melt phase volume (V_m) is assumed to remain constant, the mass balance equations for ethylhydroxy group and diester group take the following form:

$$\frac{d[E_g]}{dt} = -2(k_1 [E_g]^2 - 4k_2 [Z][\text{EG}]_m) \quad (12)$$

$$\frac{d[Z]}{dt} = k_1 [E_g]^2 - 4k_2 [Z][\text{EG}]_m \quad (13)$$

Then, eqs. (8), (9), (12), and (13) are solved together with appropriate initial conditions. The number average degree of polymerization of the polymer is calculated from

$$\bar{X}_n = 1 + 2 \frac{[Z]}{[E_g]} \quad (14)$$

Also, the total ethylene glycol removal rate from the reactor is

$$\tilde{Q}_{\text{EG}} = \int_0^t Q_g [\text{EG}]_g dt \quad (15)$$

Model Parameters

To solve the above modeling equations, the mass transfer coefficient needs to be known. From the penetration theory, the following expression is derived for mass transfer coefficient:

$$k_L = 2 \sqrt{\frac{D_{\text{EG}}}{\pi \theta}} \quad (16)$$

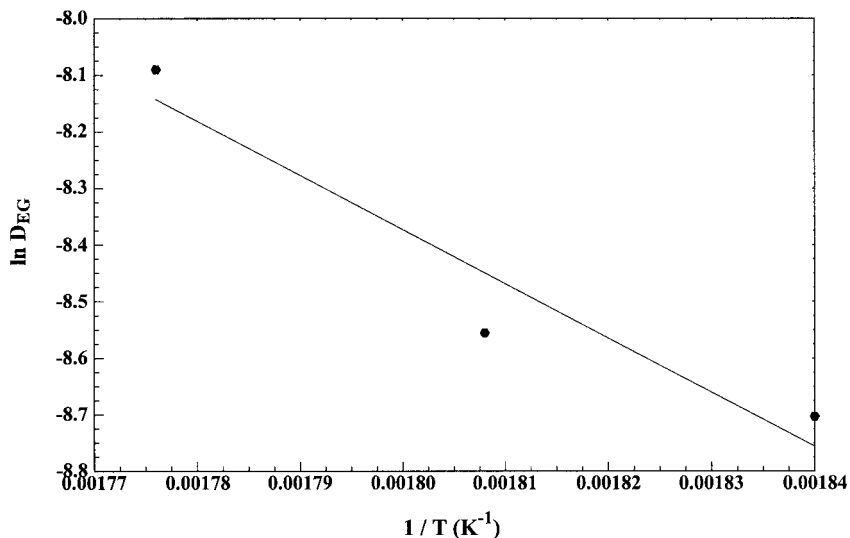


Figure 2 Diffusivity of ethylene glycol in a molten PET.

where D_{EG} is the diffusivity of ethylene glycol in the polymer melt in cm^2/s and θ is the contact time in seconds. In the penetration theory, the contact time θ represents the time for a fluid element in the bulk melt phase to be in contact with a gas phase at the gas–fluid interface. Since diffusivity is temperature dependent, the mass transfer coefficient also becomes temperature dependent.

The mass transfer coefficient values of ethylene glycol in a molten PET were obtained using the experimental data reported by Cheong and Choi.¹⁶ From their experiments where polymerization experiments were carried out at 0.5 mm Hg in a rotating disk reactor system but without disk rotation, we obtained the following mass transfer coefficients: $k_L = 1.64 \times 10^{-2}$ cm/s (270°C), 1.77×10^{-2} cm/s (280°C), and 2.232×10^{-2} cm/s (290°C). The temperature dependent diffusivity of ethylene glycol can be estimated as follows: The contact time (θ) is determined by substituting the mass transfer coefficient and the diffusivity of ethylene glycol measured by Pell and Davis¹⁷ at 270°C in eq. (16). Then, we assume that gas–liquid contact time is not affected by temperature. With the mass transfer coefficients at three temperatures and the estimated contact time, ethylene glycol diffusivities at these temperatures can be determined. The diffusivity values thus estimated are plotted in Figure 2 and the data were fitted in Arrhenius form:

$$D_{EG}(T) = 7.20 \times 10^3 \exp\left(-\frac{9.586 \times 10^3}{T}\right) \quad (\text{cm}^2/\text{s}; T \text{ in K}) \quad (17)$$

In the above, the activation energy for diffusion is 19.0 kcal/mol. Figure 2 indicates that the diffusivity changes with temperature quite substantially even in the small temperature range of 260–280°C. The diffusivity of ethylene glycol at 270°C calculated from eq. (17) is 1.56×10^{-4} (cm^2/s), which is very comparable with the experimentally measured value of 1.66×10^{-4} (cm^2/s) reported by Pell and Davis.¹⁷

The formation of gas bubbles and their behaviors in viscous liquids have been the subject of study for years by many researchers. To model the inert gas sweeping process we consider in this work, it is necessary to estimate gas holdup and interfacial mass transfer area that are dependent on bubble size, bubble rising velocity, and number of bubbles in the reactor. When gas is injected to a viscous liquid through an orifice, bubble size is a function of the orifice size at low gas flow rates. As gas flow rate is increased to a certain point, bubble formation is hindered by the presence of preceding bubbles and bubble size increases as a function of gas flow rate rather than the orifice size.¹⁸ In our experiments where the diameter of the gas injection tube was 0.318 cm, gas flow rates employed were such that bubbles were far larger than the injection tube diameter. Davidson and

Schüler¹⁹ proposed the following equation to calculate the volume of a gas bubble in a viscous liquid when the gas flow rate is Q_g :

$$V_g^* = \left(\frac{4\pi}{3}\right)^{1/4} \left(\frac{15\nu Q_g}{2g}\right)^{3/4} \quad (18)$$

where V_g^* is the volume of a single gas bubble in cm^3 , ν is the kinematic viscosity of the polymer melt and g is the acceleration of gravity (980 cm/s^2). The kinematic viscosity increases during the reaction as the polymer molecular weight increases. In deriving the above equation, Davidson and Schüler assumed the following: the bubble is spherical throughout formation; circulation of the liquid is negligible; the motion of the bubble is not affected by the presence of another bubble immediately above it; the momentum of the gas is negligible; the bubble is at all instants moving at the Stokes velocity appropriate to its size. In our polymerization system, some of these assumptions may not be exactly applicable. For example, according to our experimental observations bubbles detached from the tip of a gas injection tube are nearly spherical at low melt viscosity, but bubbles are elongated in the vertical direction as melt viscosity increases due to polymerization. The movement of gas bubble is affected by the presence of other bubbles present in the fluid. We also assume that the increase in the bubble size due to the diffusion of ethylene glycol from the melt phase is negligible because the bubble-melt contact time is quite small. We ignored the change in bubble size due to bubble breakup or coalescence. It is generally observed that bubble breakup rates decrease with an increase in liquid viscosity.²⁰ Considering all these factors, we can say that the bubble size calculated from eq. (18) is approximate.

To estimate the bubble residence time or contact time with the polymer melt phase, bubble rising velocity and gas holdup need to be estimated also. For a power law fluid, Chhabra²¹ reports that depending upon the values of the power law flow index (n) and the gas fraction, the rise velocity of a bubble swarm may be greater or smaller than the velocity of a single bubble. To calculate the bubble rising velocity (u_b in cm/s), we shall use the following correlation proposed by Snabre and Magnifotcham²² for a vertical bubble stream rising with a stationary velocity in a viscous liquid:

$$u_b = \left(\frac{2d_b g(1 + Q_g d_b / u_b V_g^*)}{C_d}\right)^{1/2} \quad (19)$$

where d_b is the bubble diameter in centimeters (assumed spherical) and C_d is the drag coefficient ($C_d = 16/Re + 1$).

The average bubble residence time or contact time (θ_b in seconds) in the reactor and the number of bubbles (N) of average residence time of θ_b are estimated from the following equations:

$$\theta_b = \frac{V_m(1 + \varepsilon_g)}{u_b S_R} \quad (20)$$

$$N = \frac{Q_g \theta_b}{V_g^*} \quad (21)$$

where S_R is the cross sectional area of the tube reactor (in cm^2) of diameter D_R . In our model, we assume that the contact time is approximately equal to the average residence time of a bubble rising in the melt phase. It needs to be pointed out that the contact time for some gas bubbles circulating in the melt phase may be longer than the average contact time. The effect of bubble circulation in the melt phase is not considered in our work. The total gas-liquid interfacial area for mass transfer is calculated using N and the bubble diameter estimated from the above equations.

The fractional gas holdup ($\varepsilon_g = V_g/V_m$) in the polymer melt is estimated by the following correlation developed for a bubble column by Godbole et al.²³ for a highly viscous fluid:

$$\varepsilon_g = 0.239(u_b)^{0.634} D_R^{-0.5} \quad (u_b \text{ in m/sec, } D_R \text{ in m}) \quad (22)$$

The numerical values of the parameters used in our reaction model are $k_1 = 9.77 \times 10^{-3} \exp(-1.34 \times 10^4/T) \text{ L/mol min}$ (T in K), $K (= k_1/k_2) = 0.5$, $m = 5$, $[E_g]_0 = 1.382 \text{ mol/L}$, $[Z]_0 = 5.528 \text{ mol/L}$, $[EG] = 0 \text{ mol/L}$.

RESULTS AND DISCUSSION

Since ethylene glycol generated by polycondensation reaction diffuses from the melt phase to nitrogen gas bubbles, the bubble rising velocity or gas flow rate is an important design parameter. In our experimental study, the effect of nitrogen gas flow rates on polymer molecular weight was

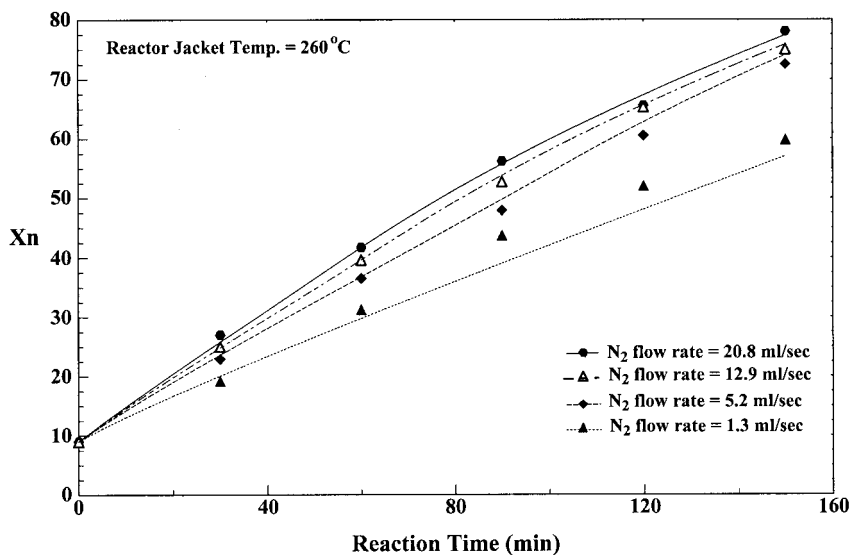


Figure 3 X_n profiles at different nitrogen gas flow rates (jacket temperature = 260°C).

first investigated. Figure 3 shows the X_n (degree of polymerization) vs reaction time profiles at four different nitrogen gas flow rates when the glass reactor jacket temperature is 260°C. The polymer molecular weight increases almost linearly with time. As gas flow rate is increased, polymer molecular weight increases accordingly. However, it is seen that the effect of increasing gas flow rate on polymer molecular weight tends to diminish, as the gas flow rate is higher than about 12.9 mL/s. The agreement between the experimental data (symbols) and the model simulation results

(lines) looks quite satisfactory, supporting the validity of the proposed mass transfer-reaction model. Figure 3 illustrates that the inert gas sweeping technique is indeed quite effective in removing ethylene glycol from the melt phase, thereby increasing the polymer molecular weight. Figure 4 shows the amount of ethylene glycol removed from the reactor during polymerization (model calculations). The measurement of ethylene glycol removed was too small to measure experimentally. Notice that although the rate of ethylene glycol removal becomes quite small after

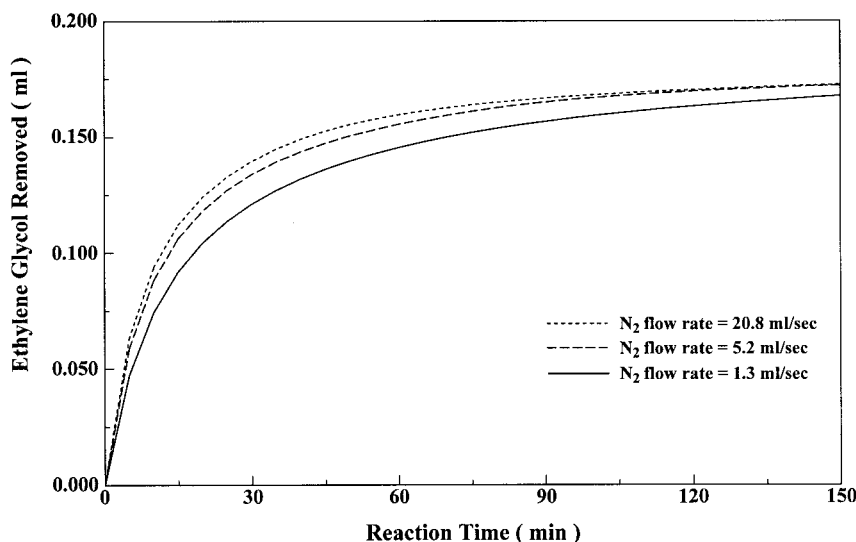


Figure 4 Amount of ethylene glycol generated by polymerization (calculated).

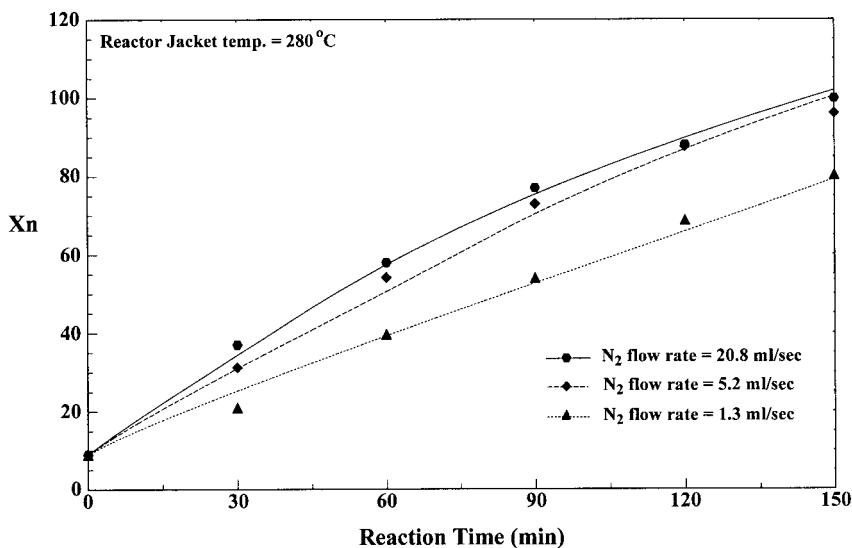


Figure 5 X_n vs reaction time at different nitrogen gas flow rates (jacket temperature = 280°C).

about 90 min, polymer molecular weight continues to increase as shown in Figure 3.

Similar experiments were carried out at higher reaction temperature and the results are shown in Figure 5. It is interesting to observe that X_n values at 280°C (jacket temperature) are consistently higher than the X_n values at 260°C (jacket temperature) by about 20 after 150 min of reaction even at different nitrogen gas flow rates. The factors that affect the molecular weight are, for example, reaction temperature, ethylene glycol diffusivity (or mass transfer coefficient), melt viscosity, and total interfacial area. Figure 6(a) shows the effect of diffusivity (or mass transfer coefficient) on X_n . If diffusivity is assumed temperature invariant and the diffusivity value at 260°C (smaller than actual diffusivity at 280°C) is used to simulate the polymerization at 280°C with nitrogen gas flow rate of 1.3 mL/s, the predicted molecular weight (solid line) is much lower than experimentally observed. It implies that the polymerization is strongly mass transfer limited. However, when the nitrogen gas flow rate is increased to 20.8 mL/s, as shown in Figure 6(b), the effect of diffusivity becomes relatively unimportant.

At this point, it would be worthwhile comparing the current experimental results with those obtained by conventional high vacuum processes. Figure 7 shows X_n vs time profiles when polymerization was carried out at 0.5 mm Hg and 280°C in a laboratory scale semibatch rotating disk re-

actor of length 15 cm.¹⁶ Although the prepolymer molecular weights in both experiments are slightly different, we can make a qualitative or semiquantitative comparison. It is seen that the rate of increase in X_n in the vacuum process with 12 disks is quite similar to that in the inert gas sweeping process at ambient pressure. In the high vacuum process, the rotating disks refresh the interfacial surface area, whereas in the inert gas sweeping process, the continuously injected inert gas bubbles rising through the molten polymer refresh the interfacial area.

It has been observed in our experiments that a swarm of small gas bubbles (approximately spherical) flow through the melt phase during the early period of reaction, but as the melt viscosity increases due to polymerization, the number of bubbles decreases and the size of the bubble increases. Also, the detachment time for a gas bubble from the tip of the injection tube increases. The bubbles at high melt viscosity are deformed significantly in vertical direction. In our model calculations, the maximum bubble diameter was set at the tube diameter. Although gas bubbles are not spherical when bubble size reaches its maximum, the correlations [eqs.(18)–(22)] developed for spherical bubbles were assumed valid. Figure 8 shows how the bubble diameter increases with reaction. Notice that at 280°C the bubble diameter reaches 1.8 cm (reactor tube diameter) after about 20 min. Figure 9(a) shows the computed bubble rising velocity and Figure

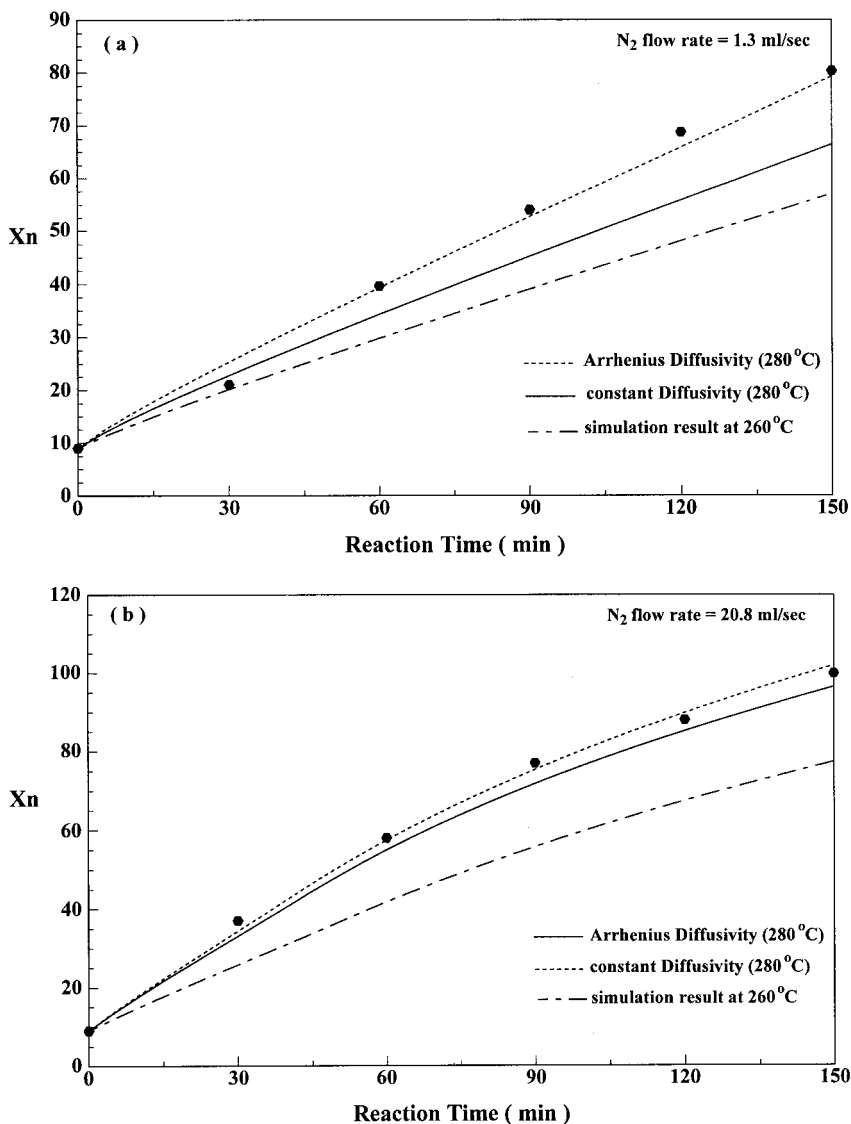


Figure 6 Effect of temperature dependent diffusivity of ethylene glycol on X_n .

9(b) shows the melt viscosity at different gas flow rates. The decrease in the number of gas bubbles with an increase in conversion or molecular weight is illustrated in Figure 10 (calculation). Notice that only a few bubbles are present near the end of polymerization. In our experiments, we indeed observed such a small number of bubbles at high conversion.

In our experiments, we observed a large number of tiny bubbles present in the polymer melt during the polymerization. Some of these small bubbles might have been formed by the breakup of injected nitrogen gas bubbles or by the nucleation of ethylene glycol bubbles. Han and Han²⁴ report that bubble nucleation in a viscous poly-

mer melt can be induced either by flow and/or shear stress at an unsaturated condition. When nitrogen gas bubbles rise through the viscous polymer melt in our experiments, these bubbles cause the circulation of the polymer melt, generating a shear force in the reactor. Thus, it is believed that the flow of gas bubbles induce the nucleation of ethylene glycol bubbles. To investigate the bubble nucleation phenomena in the polymer melt, we carried out a simple experiment: As prepolymer was polymerized without injecting nitrogen gas at 280°C, a small number of tiny bubbles were observed in the melt phase but the entire polymer melt was clear. Then, as the reaction tube was shaken by hand several times,

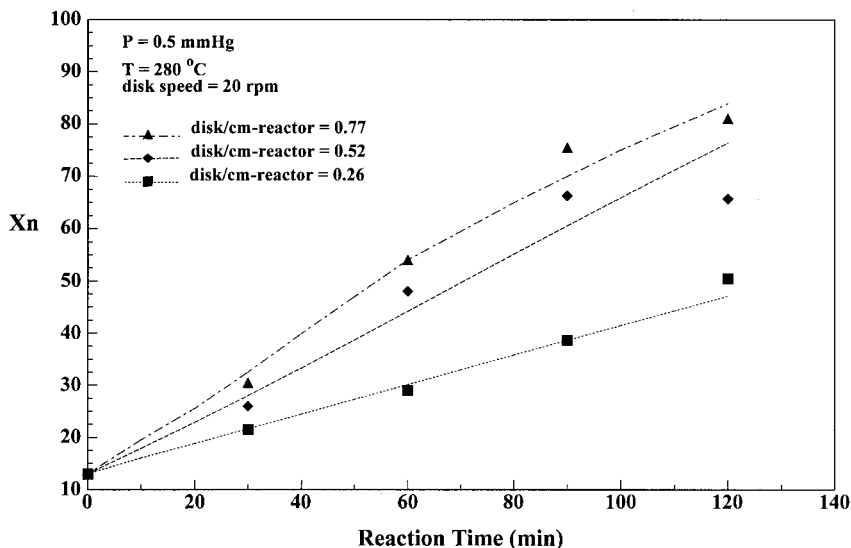


Figure 7 High vacuum semibatch melt polycondensation of PET in a rotating disk reactor for different numbers of disks [4 disks (0.26 disk/cm reactor), 8 disks (0.52 disk/cm reactor), and 12 disks (0.77 disk/cm reactor)].¹⁶

the whole polymer melt was quickly saturated with very small gas bubbles. This simple experiment suggests that tiny bubbles are formed even without breakup of injected nitrogen gas bubbles.

We also investigated the presence of nucleated ethylene glycol bubbles during normal gas sweeping process as follows. After polymerization, the reaction tube was removed from the heating jacket assembly and quenched rapidly to freeze any gas bubbles trapped in the polymer. Figure

11 shows the scanning electron microscopic picture of the PET polymer recovered from the reactor. We can see that there are many cavities of size of about 100–400 μm . Since nitrogen gas bubbles are much larger than the cavities shown, it is believed that these cavities were formed by the nucleation of ethylene glycol bubbles in the polymer melt.

Although the nucleation of ethylene glycol bubbles was observed in our experiments, the effect of

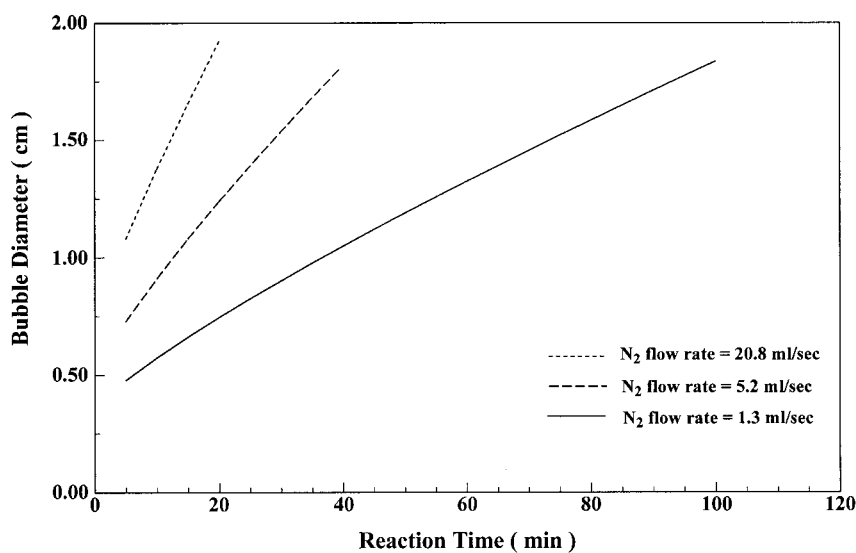


Figure 8 Bubble diameters at different gas flow rates (calculated) (jacket temperature = 280°C).

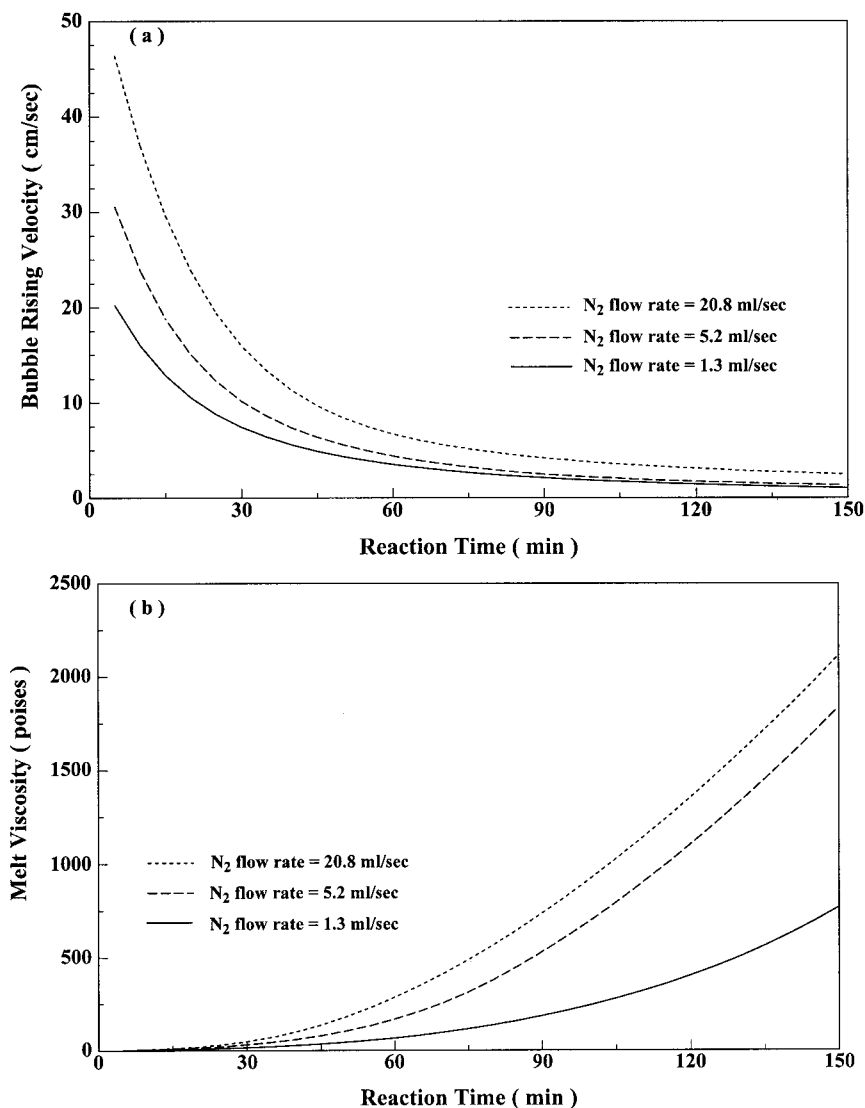


Figure 9 Effect of gas flow rate on bubble rising velocity and polymer melt viscosity (jacket temperature = 280°C).

such bubbles on the mass transfer and polymerization rate was ignored in our modeling. To examine the effect of nucleated ethylene glycol bubbles on polymerization rate, we carried out the following experiment. Without nitrogen gas flow, the polymer melt in the reactor was agitated mechanically by a thin stainless steel wire. Again, the nucleation of a large number of very small bubbles was observed. A small amount of polymer sample was taken for analysis at every 30 min during the reaction. However, it was found that the increase in polymer molecular weight was almost negligible even after 150 min of reaction at 280°C. This experimental result suggests that the presence of nucleated ethylene glycol bubbles has

little influence on the polymerization rate or polymer molecular weight unless they are removed either by vacuum or inert gas.

CONCLUDING REMARKS

In this paper, new experimental results have been presented on the polymerization by forced gas sweeping process. Our experimental investigation strongly suggests that the gas sweeping process operating at ambient pressure is as effective as high vacuum melt processes to obtain high molecular weight poly(ethylene terephthalate). A

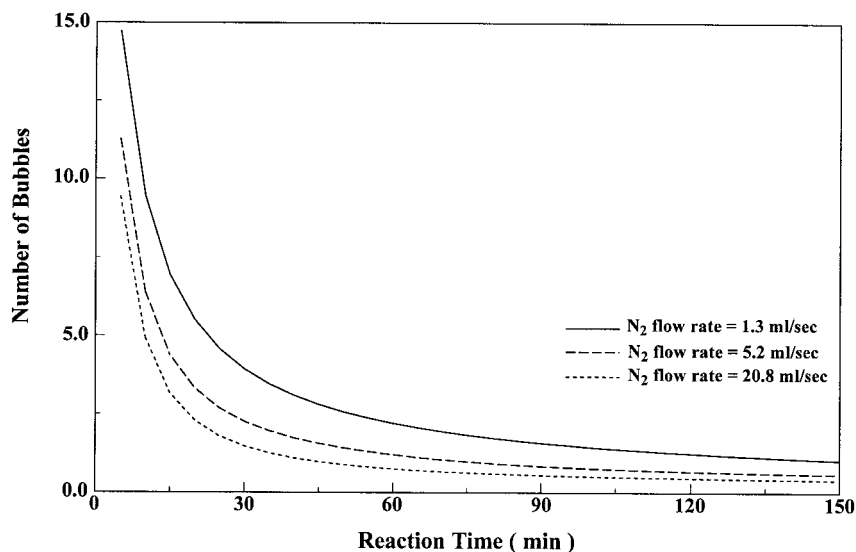


Figure 10 Number of gas bubbles (calculated) at different gas flow rates (jacket temperature = 280°C).

mass transfer-reaction model has also been developed and the model provides adequate prediction of the reaction process. For model simulations, various theoretical and empirical correlations reported in literature have been used. These correlations are needed to estimate, for example, average bubble residence time, fractional gas holdup, and bubble rising velocity. The accuracy of model predictions may depend on the quality of such correlations; however, once these correlations are in place no model parameters need to be adjusted. It was observed that polymerization rate was strongly influenced by nitrogen gas flow rate, but

there seemed to be a critical gas flow rate above which its effect became negligible. The effect of nucleated ethylene glycol bubbles was examined experimentally and the presence of ethylene glycol bubbles had a practically negligible impact on the polymerization rate or molecular weight.

Although there are some limitations in the experimental results reported in this work in that the polymerization experiments were carried out in a small diameter glass tube reactor with a relatively small amount of polymer melt, the data and the model simulation results indicate that the forced gas sweeping technique can be developed to a feasible alternative to high vacuum melt polycondensation processes.

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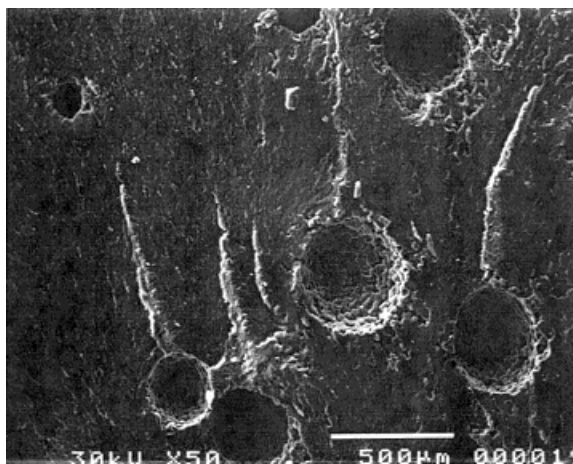


Figure 11 Scanning electron micrograph picture of PET showing gas cavities.

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